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Evidence of memory effects in a commensurate ferroelectric phase

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Dielectric measurements in $[N(CH_3)_4]_2CoCl_4$ crystals are reported that show that memory effects in materials exhibiting incommensurate phases are not exclusively limited to these phases but can also appear in commensurate ones. The dielectric susceptibility of the material suffers strong anomalies in the ferroelectric commensurate phase after annealing in this phase for a few hours. The characteristics of this new effect are more complex than those previously reported within incommensurate phases.

Since the first results about kinetic effects in incommensurate (IC) ferroelectrics,[1-4] it has gradually become clear that these effects principally involve the following.

(a) Anomalous thermal hysteresis, which is reflected in different cooling and heating curves of macroscopic and microscopic magnitudes in a large-temperature interval around the IC-ferroelectric (lock-in) phase transition. These systems behave differently when cooling or heating runs are reversed even without crossing the lock-in transition.

(b) Memory effects associated with annealing times of a few hours in the IC phase and characterized by a small kink centered at the annealing point on the corresponding heating (cooling) curve and a similar anomaly on the cooling (heating) run but centered at a different temperature, which is apparently related to the original annealing point through the observed thermal hysteresis.[2,5,6] Much stronger memory effects have been observed also in $Ba_2NaNb_5O_{15}$.[7]

In the case of thermal hysteresis, the relative importance of extrinsic and intrinsic causes is not yet clear.[4,8,9] Although experimental results show that the existence of extrinsic defects strongly increases the observed effect,[1,2,10,11] it seems that the nature of the IC structure and the temperature dependence of its wavelength are enough to justify a strong anomalous thermal hysteresis in a pure crystal.[4,8] In contrast, the mentioned memory effects can be scarcely understood if the existence of extrinsic agents is not considered. In fact, the only successful approach up to now to describe these effects is provided by the "defect-density-wave" model.[5] According to it the memory effect is caused by pinning of the modulation wavelength by mobile defects coupled to the modulation. These defects are assumed to diffuse during the annealing and form a so-called defect-density wave (DDW) whose wave vector is twice that of the modulated distortion. When the crystal is removed from the annealing temperature, the DDW remains due to the slow mobility of the defects. Subsequently the DDW will try to lock the modulation wave vector into the value corresponding to the annealing point whenever the system approximates the configuration of the annealing temperature. In other words, the DDW created during the annealing introduces an additional lock-in term in the crystal free energy, which favors the modulation wavelength of the annealing configuration with respect to its neighboring values. Thus, it creates an artificial lock-in phase, whose range will increase with the annealing time. Deuterated thiourea[3,5,12,13] is the material where this model has been specially checked. Despite its success it must be noted that the DDW model has not yet been confirmed with microscopic measurements and it is not clear how the DDW can lock the modulation wavelength without simultaneously reducing the local mobility of the modulation with the consequent decrease of the dielectric susceptibility.

According to the DDW model it was expected that memory effects should only appear in IC phases since only in this case does the modulation wave vector vary continuously with temperature in a nontreated sample. Contrary to this assumption, we report in this Brief Report the first evidence of the existence of a strong memory effect in a ferroelectric commensurate phase. The present study was carried out in high-quality $[N(CH_3)_4]_2CoCl_4$ crystals. This material (here indicated as $TMACoCl_4$) shows a sequence of modulated phases characterized by a structural modulation with a wave vector $q=\delta c^*$ with δ taking several commensurate and incommensurate values.[14,15] Seven different phases are observed, and the four phase transitions involved here take place in the temperature interval 0–25 °C. Let us call these phases I, II(IC), III(F), IV(IC), V, in decreasing temperature, where (F) and (IC) indicates that the corresponding phase is ferroelectric and incommensurate, respectively. The ferroelectric phase extends in a temperature range of 3.5 K, approximately, and it is sandwiched between two incommensurate phases, so that on heating or cooling the system arrives at the ferroelectric phase through a previous incommensurate one. A complete characterization of the different phases and transition temperatures was given by Sawada, Yamaguchi, Suzuki, and Shimizu.[16] In order to be consistent with these authors, the II(IC)→III(F) and III(F)→IV(IC) transition temperatures will be referred to as $T_c^{(u)}$ and $T_c^{(l)}$, respectively.

Measurements of the modulus of the dielectric susceptibility were performed in the temperature range 0–25 °C, that is, between phases I and V. The experimental-device accuracy and crystal quality are described elsewhere.[6] As indicated there, special precautions have been taken in the temperature-control system to ensure a temperature stability better than 0.1 K. In the following the measured susceptibility values will be given in relative units with respect to the vacuum dielectric permittivity.

Figure 1 shows the heating and cooling dielectric-susceptibility curves corresponding to the I to V transition sequence for a TMACoCl$_4$ crystal previously annealed for 24 h in phase I. It must be noted that we need these curves in order to have a correct baseline and, therefore, they were measured every time a new memory effect was written up in the sample or when a new crystal was used.

The new memory effect was studied according to the following procedure: A sample was annealed at a temperature $T^* < T_c^{(u)}$ on the cooling run (point A in Fig. 2) for some hours. During this time the measurement system was kept working and a small relaxation in the dielectric susceptibility was detected. The sample was then cooled towards the low-temperature commensurate phase V and then heated up to the high-temperature phase I. No anomalous effect other than a reduction in the peak height of the IV → III transition was then observed. But on cooling the sample again, a great anomaly appeared at the II → III transition peak. This effect persists after posterior heating and cooling runs and can be erased by setting the sample at the high-temperature phase I. Figure 2 shows the effect described above in four different samples. Similar measurements with analogous results were performed for different annealing temperatures. From these experiments the following features can be noticed.

(a) Although annealing times for the curves in Fig. 2 have been of at least 5 h, a time of about 2 h is sufficient for the effect to be clearly observed.

(b) Relaxation times of the dielectric susceptibility during the annealing were about 2 h. During this process the dielectric-susceptibility value decreases 6% to 15% depending on the sample, being greater for samples with sharper peaks.

(c) The height of the small peak in the anomaly, compared with the original transition peak, is almost independent of the annealing temperature and depends on the sample.

(d) The form of the anomaly is also sample dependent and seems to be more pronounced for samples with broader peaks.

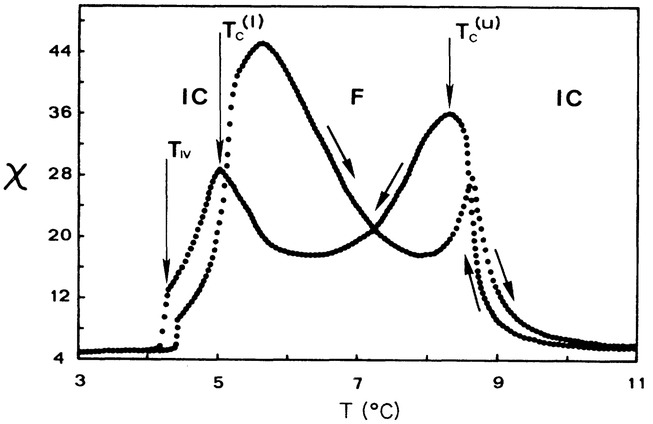

FIG. 1. Dielectric susceptibility vs temperature in a heating and cooling run for a virgin sample.

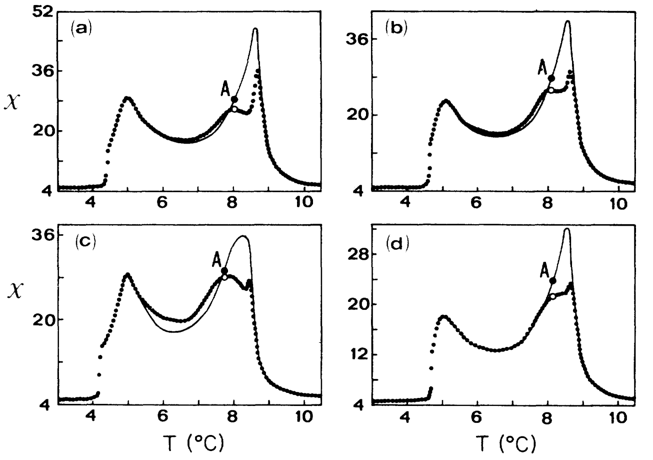

FIG. 2. Anomalies of the dielectric susceptibility observed in the cooling curve for four different samples. ●, annealing point; ○, annealing point after relaxation. Annealing times were ≃10 h [(a) and (c)] and ≃5 h [(b) and (d)]. The solid curve indicates the normal behavior.

(e) The cooling curve always passes through the annealing point.

(f) The effect of the annealing extends also to the IV → III large transition peak by a decrease in its height, which was found to be 12% to 30% for different samples.

(g) The lower peaks, that is, the ones observed when the ferroelectric phase is exited, did not suffer any essential change, although a decrease (of about 6%) has been observed in some samples at the III → II transition peak for heating runs starting in phase V. However, if just after the annealing the sample is heated up towards the incommensurate phase (II), the effect appears in the same form as on cooling, but with the thermal hysteresis of the nonannealed sample.

(h) No appreciable difference was observed in the resulting effect if the measurement system was disconnected during the annealing time.

The necessary time for the effect to be erased was estimated by writing up the effect in a sample with an annealing time of 15 h. Then the sample was heated up and kept in the high-temperature commensurate phase I for an hour, and then cooled again. This operation was repeated a few times; a gradual decrease of the effect was observed. In this way an erasing time of about 8 h could be estimated.

Annealings were also made at the III → II and III → IV lower transition peaks. In this case a similar memory effect to the one observed in the incommensurate phase[6] could be detected, although in this case the kink is rather weak (Fig. 3). An increase of the dielectric susceptibility value of about 10% was detected during the annealings. In addition a decrease of about 25% was also observed at the II → III and IV → III high transition peaks.

Annealings were also performed at the IV → III transition peak. The observed effect is totally analogous to the one obtained by annealing the sample at the II → III tran-

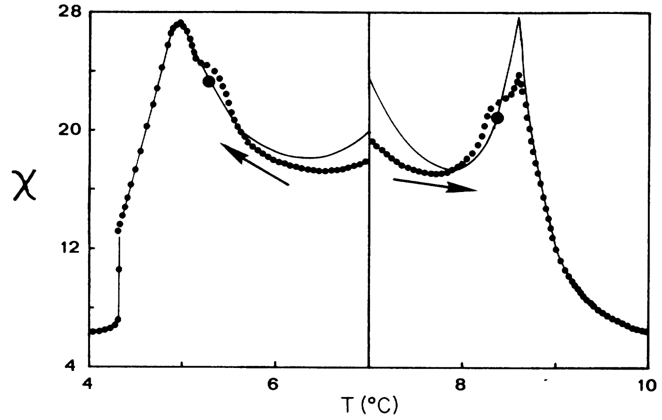

FIG. 3. Anomalies in the dielectric-susceptibility peaks corresponding to the transition III → II and III → IV after an annealing of about 15 h at the points indicated.

sition peak (Fig. 2). The corresponding decrease of the II → III transition peak was also observed.

Finally, the influence of applying a weak-bias electric field was investigated. First a sample was cooled from the high-temperature phase I and a bias electric field of 180 V/cm was applied for 30 sec just after the II → III transition peak. The effect of this field was a decrease in the dielectric susceptibility of about 20% towards a value χ^b, which remained constant after the field was removed. This value χ^b was found to be the same also if the bias field was applied for longer times (3 or 4 min). On cooling from that temperature, the observed curve tends slowly to the usual baseline and no changes were observed for subsequent heating and cooling runs. Next, a memory effect like those appearing in Fig. 2 was written up in the sample and the same electric field was then applied at the obtained anomaly during the same times. Again a decrease towards the same value χ^b was observed for the dielectric susceptibility, which also remained constant after removing the field. However, on cooling the sample again through the II → III transition the anomaly associated with the memory effect appears again in its original form. Thus, the electric field is able to eliminate the system configuration producing the anomalous behavior of the dielectric susceptibility, but not its cause since once the electric field is removed, the anomalous behavior can be observed again.

The measurements reported here clearly show for the first time the existence of a memory effect in a ferroelectric commensurate phase. This phenomenon can only be included in the framework of the DDW model if it is assumed that in the commensurate ferroelectric phase considerable regions of the crystal still remain in IC configuration, in the sense that the modulation wavelength is temperature dependent in these regions. Therefore, both phases would coexist during a considerable temperature interval of the stability range of the ferroelectric phase. The main contribution to the anomalous dielectric susceptibility is given by the IC regions and the ferroelectric domain walls. During the annealing DDW similar to those considered for the memory effect in IC phases will develop in the IC regions, while the distribution of IC and commensurate ferroelectric regions, and domain walls within the latter, will relax to a more stable configuration, giving way to the observed relaxation in the dielectric-susceptibility value. Subsequently, when cooling the sample from the IC phase the DDW localized in some parts of the crystal and produced during the annealing will originate in these regions a lock-in of the modulation wave vector to the annealing value. Out of these regions the modulation will readapt itself to compensate for these changes. It should be pointed out that in the case of TMACoCl$_4$ it is not expected that the crystal deviates from the sinusoidal regime before entering the ferroelectric phase, since after a few degrees the system reenters the IC phase. Therefore, the correlation between the configuration of the modulation in the regions with DDW and the rest of the crystal is to be specially strong. In this way, in contrast to the cases studied up to now, the annealing and the corresponding defect migration can favor inhomogeneous configurations of the modulation. This fact may explain why the dielectric anomaly reported above is much more complex than those observed when the annealing is performed in the IC phase.[6] In any case a complete understanding of the microscopic mechanism involved in this new memory effect, as well as the check of the relevance of the DDW model in it, requires further microscopic measurements.

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